Transition Metal Carbide Compounds

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INTRODUCTION

Carbon forms compounds with all the transition metals except for the late elements of the second and third rows of the periodic table. There are considerable variations in the crystal structures of these compounds. The structures of compounds formed by transition metals from the left half of the periodic table tend to be rather simple, often resembling the structure of the pure metal. Compounds formed from the right half of the periodic table, involving more electropositive elements, tend to have rather complicated structures. The compounds studied here are mainly the group IVb and Vb monocarbides, but it should be mentioned that with an increase in the ratio of metal to carbon, the compounds tend to lose stability as evidenced by decreasing melting points. A maximum in the melting points of these carbides occurs for compounds containing group Vb transition metals.[1-2] This corresponds to a filling of the bonding and anti-bonding parts of the metallic bands. The lack of stable late transition metal carbides can be explained by the filling of anti-bonding regions in the bands of these systems.[2]

EXPERIMENTAL AND CALCULATIONAL DETAILS

Due to the inherently low yield of the soft x-ray emission process, we made use of the high brightness available at Ernest Orlando Lawrence Berkeley National Laboratory's Advanced Light Source (ALS). The spectra were taken at Beamline 8.0, employing the University of Tennessee at Knoxville's soft x-ray fluorescence (SXF) endstation. At the carbon K absorption edge, the resolution of the spectrometer was approximately 0.8 eV. The energy resolution of the monochromator was set to 0.4 eV during most of these measurements. The carbon K(valence) emission spectra were calibrated with a reference sample of highly oriented pyrolytic graphite (HOPG).

In order to better understand our measurements, LMTO-ASA calculations of these carbide systems were performed. The transition metal monocarbides have face centered cubic structures, and are described by the Pearson symbol $cF8$, a member of the $Fm\overline{3}m$ (O_h^5) space group.[3] In these calculations, the exchange and correlation effects were treated by the local density approximation of density functional theory. The exchange-correlation potential formulated by Hedin and Lundquist was used to obtain self-consistent solutions to the Kohn-Sham equations.[4] The core electron states were obtained as solutions of the Dirac equations. Scalar relativistic terms were retained in the LMTO Hamiltonian for the electron band states.
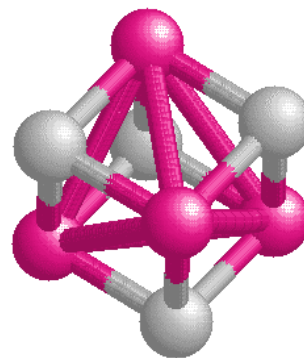
The LMTO-ASA method provides rather good

Figure 1. Image of the $Fm\overline{3}m$ cubic crystal structure of the transition metal monocarbides. Carbon atoms are depicted as the light gray spheres, metals as the dark gray spheres.

results for TiC, VC, ZrC, and NbC, but was difficult to apply to the HfC and TaC systems. Calculations of these systems were performed by Dr. James M. MacLaren from the Department of Physics at Tulane University using full potential techniques. The full potential linear augmented Slater type orbital (FP-LASTO) method eliminates any approximation made with respect to the shape of the effective single-particle potential in the crystal. The interstitial region is treated with reciprocal space techniques. A basis consisting of two sets of s, p, and d functions and a single set of f functions per atom was used for hafnium and tantalum, and a basis set of two s, two p, and a single set of d functions per atom was used for carbon. Decay constants were obtained by optimizing the basis in an atomic calculation. Electrons in the core states were treated scalar relativistically.

RESULTS AND DISCUSSION

All of the transition metal monocarbides have similar soft x-ray emission spectra. The samples were excited through the carbon K (1s) absorption threshold using the undulator and monochromator at Beamline 8.0 of the ALS. The holes left by the electrons that were excited into the conduction bands of these samples were filled with electrons from the valence bands of these materials. This allows for a confirmation of the covalent bonding detailed in the calculations of these systems.

We were able to gain knowledge from these measurements regarding the electronic structure of these carbide compounds by examining features in the soft x-ray emission spectra (SXES) of these materials. The soft x-ray emission spectra of TiC are shown in Figure 2.

Soft x-ray emission spectroscopy (SXES) can be used to examine the occupied density of states of a material. The spectrum from the sample provides an intensity versus energy distribution of the photons that are emitted during excitation. This distribution represents the density of occupied states in the material over a particular range of energies. When the emissions from valence band electron transitions are measured, bonding properties can be deduced from these valence emission spectra as the spectra are proportional to the density of states of the material. In fact, SXES can provide specific information about the angular momentum density of states of the electrons in the material, because in the case of normal fluorescence, the radiative processes adhere to the dipole selection rule. Because of this selectibility, the soft x-ray emission spectra from different electron bands can be measured and directly compared to calculations of element projected and angular momentum projected densities of states in the material.
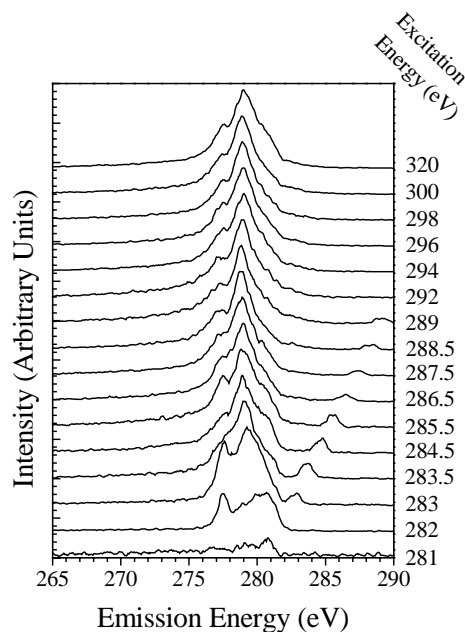

Figure 2. Soft x-ray emission spectrum of TiC. The sample is excited with photons with the energies listed to the right of the graph. The energies of the photons that are emitted from the interaction are plotted versus the number of emitted photons (intensity) that are detected by the instrument.

LMTO-ASA electronic structure calculations, as shown in Figures 3 and 4, show good agreement with the valence band emissions from the boron atoms of TiC. There have been three proposed models for describing the bonding in transition metal carbides: (1) The carbides are considered as intercalate phases. The metal-metal interaction is considered predominant with the
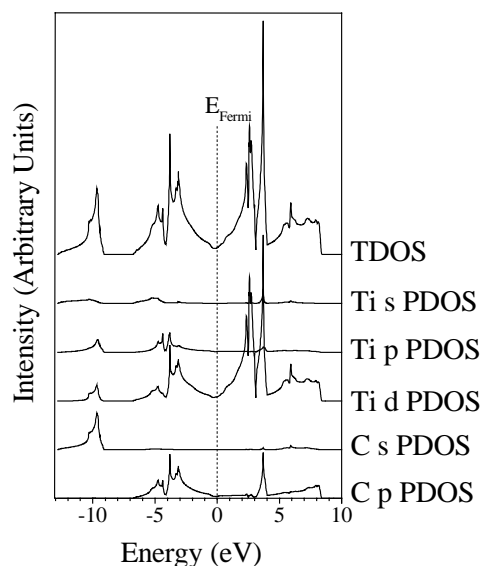
Figure 3. LMTO-ASA calculations of the electronic band structure of TiC. This material is strongly covalently bonded, with hybridization between all of the bands, especially between the titanium 3d and carbon 2p valence bands.
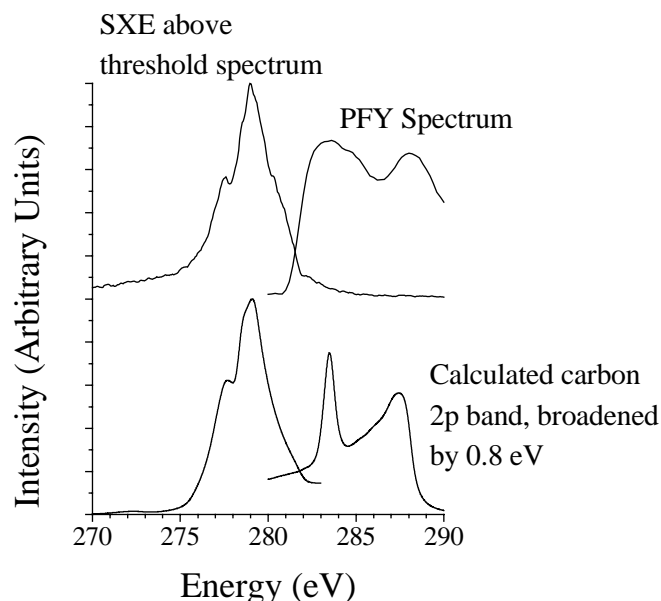

Figure 4. Comparison of above absorption threshold SXE spectra with LMTO-ASA calculations of the electronic band structure of TiC.

carbon atoms as electron donors.[2] (2) The carbon-carbon interactions are dominant since the carbides have bond lengths that are on the order of covalently bonded elemental carbon. Charge is transferred from the metal atoms to the carbon atoms.[2] (3) The covalent metal-carbon interaction is mainly responsible for the bonding of these compounds.[2] Our calculations show that the total density of states of TiC is comprised of roughly three peak structures. The lowest energy peak structure is centered around -10 eV and is composed mainly of electrons from the 2s bands of the carbon atoms and the 3p and 3d bands of titanium. The broad middle energy structure is centered around –3.5 eV and is primarily comprised of electrons from the 2p (valence) bands of the carbon atoms and electrons from the 3d (valence) and 3p bands of the titanium atoms. The sharp highest energy peak structure is centered around 3.5 eV and is primarily composed of electrons from the 3d bands of the titanium atoms, with a slight contribution from boron 2p band electrons.

From our calculations, it appears that the bonding (broad middle energy structure) and anti-bonding (sharp highest energy peak structure) states are primarily composed of carbon 2p electron bands and titanium 3d and electron bands. This suggests that the bonding in this system is primarily between carbon and titanium atoms, corresponding to a combination of two of the suggested bonding schemes for the transition metal diborides (2, and 3). TiC, and in fact all of the transition metal monocarbides are hard because of the great degrees of covalency in these materials. The densities of states below the Fermi level are almost entirely composed of contributions from the metal 3d band and the carbon 2p band. Some degree of hybridization is observed between all the metal and carbon bands in TiC. Our results are in excellent agreement with calculations of this same system made by other researchers, as well as early experiments of this compound.[5, 6-12]

CONCLUSION

From our measurements and calculations, it appears that the bonding (broad middle energy structure) and anti-bonding (sharp highest energy peak structure) states in these compounds are primarily composed of carbon 2p electron bands and metal d electron bands. This suggests that the bonding in this system is primarily between carbon and metal atoms, corresponding to a combination of two of the suggested bonding schemes for the transition metal diborides (2, and 3). All of the transition metal monocarbides are hard because of the great degrees of covalency in these materials. The density of states below the Fermi level are almost entirely composed of contributions from the metal d bands and the carbon 2p band, however, some degree of hybridization is observed between all the metal and carbon bands in these materials. Our results are in excellent agreement with calculations of these same systems made by other researchers, as well as early experiments of these compounds.

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